DOMESTIC WASTEWATER TREATMENT USING ACCELERATED OXIDATION

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ABSTRACT

The conventional treatment of wastewater is a cumbersome process involving time, energy, and space. Rapid developments have led to the search for newer techniques that can reduce these requirements and yet provide similar levels of treatments. Use of chlorine in conventional treatment leads to formation of disinfection by-products such as trihalo-methanes and halo-acetic acids that are carcinogenic. Some of the methods of preventing the formation of disinfection by-products are to remove known precursors, avoid excess chlorination, or to select an alternate method of disinfection. This paper aims to provide a solution by using ozone and hydrogen peroxide as Advanced Oxidation Process (AOP). Use of ozone and hydrogen peroxide eliminates the formation of carcinogenic disinfection by-products observed when using chlorine.

The effects of ozonation and hydrogen peroxide on parameters namely Dissolved Oxygen (DO), Chemical Oxygen Demand (COD**)**, Biochemical Oxygen Demand (BOD**)**, Total Dissolved Solids (TDS) and Suspended Solids (SS), hardness, chlorides and turbidity were studied for four different sites. Tests were performed for time periods varying from 2 to 25 minutes for ozone and up to 120 minutes in 30 minutes intervals for hydrogen peroxide. The improvement in the parameters were quantified using Water Quality Index (WQI). The values of Weighted Arithmetic Water Quality Index (WAWQI) and National Sanitation Foundation Water Quality Index (NSFWQI) were calculated and compared as a measure of improvement in the quality of treated water using ozone and hydrogen peroxide.

Key words: Ozonation, Hydrogen peroxide, wastewater treatment, AOP, WQI, WAWQI, NSFWQI

Chapter 1. INTRODUCTION

1.1 General

The world today is grappling with the challenges of the three P's: pollution, population, and poverty. Waste disposal and pollution are closely connected, with pollution referring both to the act of contaminating the environment and the harmful effects that follow. Waste generally refers to unwanted materials that are often seen as having no value. Pollution occurs when humans introduce substances, materials, or energy into the natural environment that can pose risks to human health, harm ecosystems and wildlife, damage buildings, or disrupt the natural use and beauty of the surroundings.

Ultimately, both waste and pollution contribute to a cycle of environmental degradation that affects all aspects of life. Wastewater is "used water from any combination of domestic, industrial, commercial or agricultural activities, surface runoff or stormwater, and any sewer inflow or sewer infiltration". These issues have led to the degradation of water bodies like lakes, rivers, and coastal areas, turning them into repositories for sewage and waste. As a result, the ecological balance of these ecosystems has been severely disturbed, and in some instances, completely disrupted. The harmful impact of waste on inland water systems has become particularly pronounced due to their longstanding use as dumping grounds for effluents both domestic and industrial.

Industrialization and urbanization have led to increase in volumes of wastewater generated. An increase in population and subsequent increase in the quantity of waste produced has led to failure of this mechanism and in pollution of water bodies. Absence of water bodies led to disposal on land which resulted in similar pollution of land and ground water table due to leeching. Treatment of this wastewater was introduced to reduce the effects of pollution. The objective of treatments could be listed as: removal of floating/suspended particles, removal of bio-chemical oxygen demand (BOD) and removal of pathogens (Witcher, 2016).

Various constituents of wastewater can be listed as pathogen and non-pathogenic organisms, organic and inorganic particles, soluble organic and inorganic material, animals, gases, emulsions, various macro solids and toxins. A typical wastewater treatment plant (WTP) should be able to remove these so as to have an effluent which is safe enough to be disposed in either water or on land without any harmful effect to humans which may use the water on the downstream side or aquatic life which may be present. The various steps of treatment in a WTP can be listed as follows:

- Preliminary treatment refers to use of screens or filters to remove the floating and suspended matter present in the water. Large particles like sanitary napkins, condoms, diapers, children's toys, dead animals or plants, grit and metal are some examples of materials removed during this step.
- Primary treatment consists of temporarily holding the sewage in a quiescent basin where heavy solids can settle to the bottom while oil, grease and lighter solids float to the surface. The settled and floating materials are removed and the remaining liquid may be discharged or subjected to secondary treatment. Some sewage treatment plants that are connected to a combined sewer system have a bypass arrangement after the primary treatment unit. This means that during very heavy rainfall events, the secondary and tertiary treatment systems can be bypassed to protect them from hydraulic overloading and the mixture of sewage and stormwater only receives primary treatment.
- Secondary treatment removes dissolved and suspended biological matter. Secondary treatment is typically performed by indigenous, water-borne micro-organisms in a managed habitat. Secondary treatment may require a separation process to remove the micro-organisms from the treated water prior to discharge or tertiary treatment. Generally, about 50% of the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are removed as a part of the settled solids.
- Tertiary treatment is sometimes defined as anything more than primary and secondary treatment to allow ejection into a highly sensitive or fragile ecosystem (estuaries, low-flow rivers, coral reefs etc.) Treated water is sometimes disinfected chemically or physically (for example, by lagoons and microfiltration) prior to discharge into a stream, river, bay, lagoon or wetland, or it can be used for the irrigation of a golf course, green way or park. If it is sufficiently clean, it can also be used for groundwater recharge or agricultural purposes.

Since 1990s, there has been a better understanding of the long-term effects of wastewater on human health and the environment. Due to this, the effluent standards have been made more stringent not only for industrial effluents but also for domestic or municipal wastewaters (Bakkaloglu et al., 1998). The main aim being to achieve reduction in toxic and potentially toxic chemicals in the environment.

1.2 Need for this study

There has been a rapid increase in global population in the recent decades. This has led to increased wastewater generation. A quicker method of treatment of wastewater is the need of the

hour in order to ensure that all the wastewater generated is treated to safe limits before being discharged into the water bodies. Certain reasons necessitating this study are explained in brief below:

*Increase in volume coupled with shortage of space***:** Due to rapid increase in population, there has been a great increase in the amount of wastewater being generated. Rapid industrialization has also deteriorated the quality of effluent being generated in addition to the volume being increased. Due to this, the present WWT plants are not able to handle the increased volumes effectively. Also, land is not as freely and cheaply available as earlier hence, construction of more number of treatment units is becoming increasingly difficult.

*Rising cost of energy***:** Most of the treatment plant designed earlier did not pay sufficient attention to the amount of energy being consumed as it was not very important. With the increase in cost of fuel and subsequent increase in the cost of energy, it has become imperative to reduce the amount of energy consumed in the entire water treatment process.

*Environmental concerns***:** As more energy is being consumed, the consumption of fossil fuel is increasing. This leads to an increase in the amount of greenhouse gases being released into the atmosphere. This necessitates search for methods which will require lesser energy than the conventional methods and also release lesser amounts of greenhouse gases.

Conventionally chlorine was used for disinfection of wastewater because it of its effectiveness, residual properties, and low cost. During the 1970s, the harmful effects of chlorine came into light. Formation of carcinogenic disinfection by-products which affected human and aquatic life was a major reason why alternate measures were being sought out. (Lazarova et al., 2000)

Advanced oxidation processes (AOPs) were initially introduced in the 1980s for treating drinking water and have since been extensively researched for the treatment of various types of wastewater. In wastewater treatment using AOPs, hydroxyl radicals (OH·) or sulphate radicals ($SO4^{\cdot -}$) are produced in sufficient amounts to degrade persistent organic substances, trace organic pollutants, and certain inorganic contaminants. Additionally, AOPs can enhance the biodegradability of wastewater, serving as a pre-treatment step before subsequent biological treatment (Deng & Zhao, 2015). A wide variety of AOPs are available as shown in Figure 1.1 These methods are used worldwide for groundwater treatment, for drinking water and process water treatment, and for removal and disinfection of organic matter from industrial wastewater.

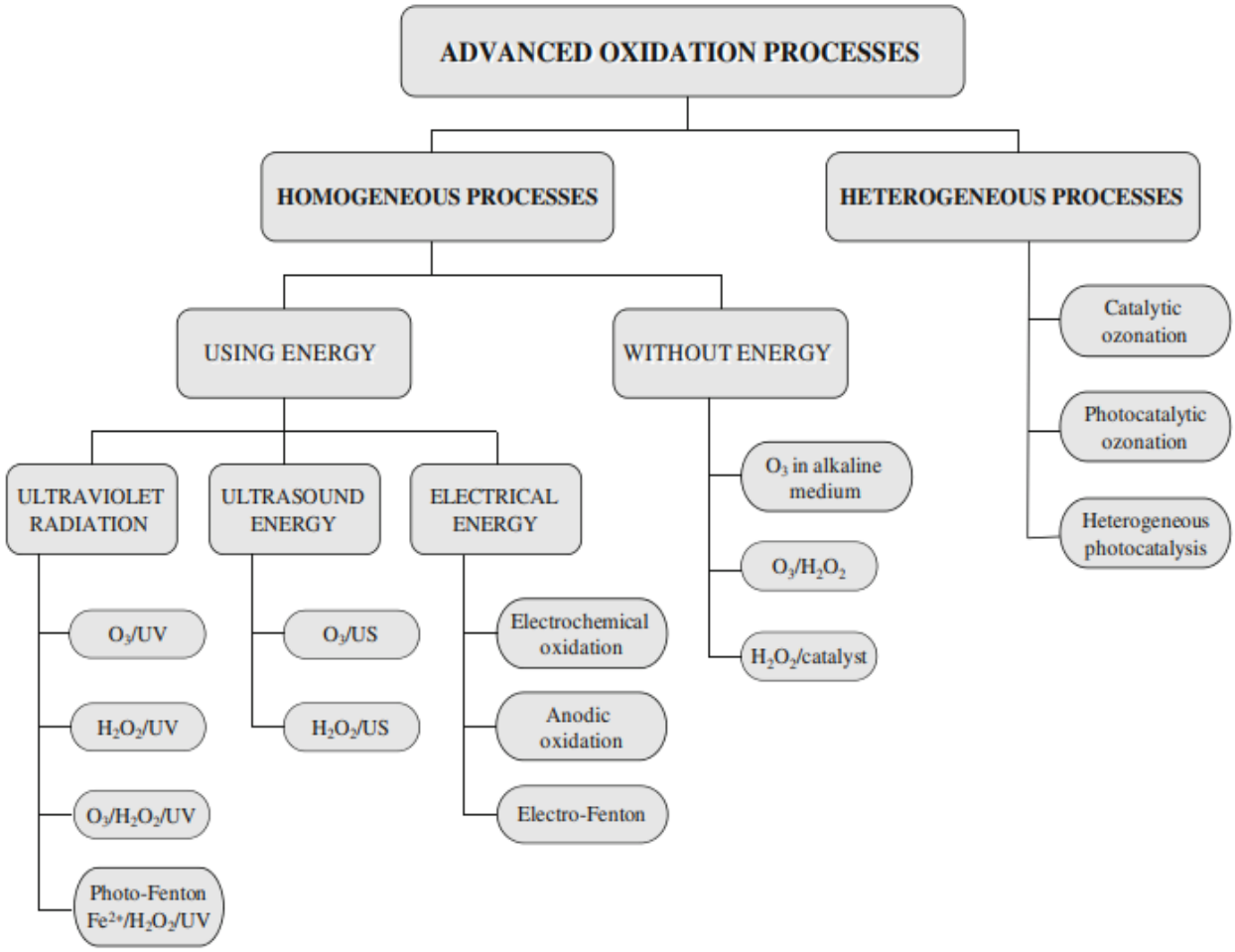

Figure 1.1 Classification of Advanced oxidation processes (AOPs). Abbreviations used: O_3 - ozonation; H_2O_2 - hydrogen peroxide; UV- ultraviolet radiation; US - ultrasound energy; Fe^{2+} - ferrous ion (Poyatos et al., 2010).

AOPs offer many advantages, some of which are as follows: They have rapid reaction rates but small footprints. They do not lead to formation of new hazardous substances as in the case of chlorination. They can treat almost all organic materials and certain heavy metals too. There is no issue of sludge formation as seen in the case of chemical or biological processes due to which sludge disposal is not required. It may be noted that sludge disposal is generally done on drying beds which is another source of land pollution and hence is a very important factor favouring this method. Despite these, there are certain disadvantages associated with the use of AOPs namely relatively high capital and operating costs involved. The chemistry has to be tailored according to the contaminants present in the wastewater and a universal method is not possible. Also, the removal of residual peroxide adds up another step to the treatment process.

For this study, use of ozone and hydrogen peroxide as stand-alone methods of AOP has been considered. Ozone is easily manufactured on site by using an ozone generator which converts

atmospheric oxygen into ozone by means of electric spark. Hydrogen peroxide is easily available as an industrial or laboratory grade chemical reagent. The method of treatment using these two agents is simple and did not require any elaborate set-up.

1.3 Ozone as a disinfectant

Ozone is the allotropic form of oxygen which is triatomic and hence unstable at normal temperature and pressure decomposing into molecular oxygen. It is a very powerful oxidant, with a redox potential of 2.07V and has many commercial and industrial applications (Mota et al., 2008, (Hoigne, 1998). It is used commonly in potable and non-potable water treatment, and as an industrial oxidant. As it has a considerable oxidizing power and molecular oxygen as its by-product, it becomes an obvious choice for oxidation and disinfection. Ozone has been widely used for treatment of drinking water and its disinfection since 1906 in Paris, France; though using it for wastewater started much later.

Ozone disinfection works through the following mechanisms:

- Direct oxidation or breakdown of the cell wall, resulting in the release of cellular components outside the cell.
- Reactions with ozone decomposition's radical byproducts.
- Breakage of carbon-nitrogen bonds leading to depolymerisation.
- Damage to the purines and pyrimidines that make up the nucleic acids.(US EPA, 1999)

When ozone decomposes in water, the free radicals of hydrogen peroxy (HO_2) and hydroxyl (OH^-) that are formed have great oxidizing capacity and play an active role in the disinfection process. It is generally believed that the bacteria are destroyed because of protoplasmic oxidation resulting in cell wall disintegration (cell lysis).

1.3.1: Advantages and disadvantages

The main advantages of using ozone can be listed as follows:

- Ozone is more effective than chlorine in destroying viruses and bacteria.
- The ozonation process utilizes a short contact time (approximately 10 to 30 minutes).
- There are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly.
- After ozonation, there is no regrowth of microorganisms, except for those protected by the particulates in the wastewater stream.
- Ozone is generated onsite, and thus, there are fewer safety problems associated with shipping and handling.

- Ozonation elevates the dissolved oxygen (DO) concentration of the effluent. The increase in DO can eliminate the need for reaeration and also raise the level of DO in the receiving stream.

But use of ozone has certain drawbacks also. These can be listed as follows:

- Some viruses, spores, and cysts may not be properly inactivated by low dosages.
- Ozonation is a more complex process than UV or chlorine disinfection, requiring sophisticated equipment and good contacting systems.
- Because ozone is highly reactive and corrosive, materials that are resistant to corrosion, like stainless steel, are necessary.
- Wastewater with high amounts of suspended solids (SS), chemical oxygen demand, biochemical oxygen demand (BOD), or total organic carbon is not cost-effective for ozonation.
- The cost of treatment can be somewhat significant in terms of capital and power intensity.
- In order to prevent worker exposure, off-gases from the contactor must be destroyed as ozone is highly irritating and potentially hazardous.(US EPA, 1999)

The increasing popularity in recent years concerning ozone applications are mainly due to two factors (i) costs associated with ozone production has considerably decreased in the last decade and (ii) ozone presents environmental advantages over chlorine.

1.4 Hydrogen peroxide as a disinfectant

In the environment, hydrogen peroxide can be found in very low concentrations. Gaseous hydrogen peroxide is produced by photo-chemical reactions in the atmosphere surrounding the earth. It is available as a liquid in 50% and 30% concentrations industrially. It has a redox potential of 1.77 V as compared to 2.07 V of ozone (Mota et al., 2008). The disinfection mechanism of hydrogen peroxide is based on the release of free oxygen radicals. Free radicals have both oxidising and disinfecting abilities. The free oxygen radical decomposes the pollutants leaving only water behind.

1.4.1 Advantages and disadvantages

The main advantages of using hydrogen peroxide is as follows:

- Hydrogen peroxide is a potent oxidising agent that can break down a variety of organic contaminants, such as industrial chemicals, dyes, and medications.
- It produces hydroxyl radicals, which are extremely reactive and effective at decomposing pollutants.

- Hydrogen peroxide is a green wastewater treatment option because it breaks down into water and oxygen and doesn't produce any hazardous byproducts.
- It is adaptable to many wastewater types since it may target a wide range of contaminants.
- Hydrogen peroxide is simple to use, store, and apply.
- To improve treatment effectiveness, it is frequently combined with additional procedures like UV or Fenton reactions.

The main disadvantages of using hydrogen peroxide are:

- Using hydrogen peroxide can be more costly than using alternative treatment techniques, particularly if large dosages are needed to completely degrade the contaminants.
- If improperly handled or stored, it may become unstable and breakdown, making it difficult to retain its efficacy over time.
- Although hydrogen peroxide decomposes into oxygen and water, partial reactions may result in the creation of intermediate chemicals that need additional care.
- The pH of the wastewater can affect how well hydrogen peroxide works as an oxidant, hence careful pH control is required during treatment.(Pandis et al., 2022)

1.5 Water Quality Index (WQI)

Water quality index is a concept used to describe the quality of surface waters. Various parameters are combined into single value ranging from 0-100. There are four most common methods which are used for the calculation of WQI are as follows:(Chidiac et al., 2023)

1. National Sanitation Foundation Water Quality Index (NSFWQI),
2. Canadian Council of Ministers of Environment Water Quality Index (CCMEWQI),
3. Oregon Water Quality Index (OWQI), and
4. Weighted Arithmetic Water Quality Index (WAWQI)

In this study, WQI has been used as a measure for improvement in the parameters after wastewater treatment. In order to quantify the improvement in the parameters tested, WQI of the wastewater is calculated by using WAWQI and NSFWQI methods for both ozone and hydrogen peroxide.

Based on the literature studied and in order to introduce this concept, the last objective of this study was modified from “To develop domestic wastewater treatment method using accelerated oxidation process based on above results” to “To compare the effectiveness of treatment using WQI” as listed on the next page.

Chapter 2. OBJECTIVES

The objectives of this study can be listed as follows:

- **Objective 1:** To assess the effect of oxidation on various parameters like BOD, COD, DO, hardness, turbidity, pH of raw sewage.
- **Objective 2:** To evaluate the effect of using ozone on various parameters
- **Objective 3:** To evaluate the effect of using hydrogen peroxide on various parameters.
- **Objective 4:** To compare the effectiveness of treatment using WQI.

Chapter 3. LITERATURE REVIEW

3.1 Introduction

This work deals with using accelerated oxidation as a stand-alone process for the treatment of wastewater. This study is divided into three parts; first is using ozone as an AOP, second using hydrogen peroxide as an AOP and finally the use of WQI to compare the effectiveness of both the methods. The first part of literature review deals with the treatment of wastewater in general, the second part deals with the use of ozone and hydrogen peroxide as a means of AOP whereas the third part deals with the use of WQI.

3.2 Wastewater treatment

The increase in water stress due to climate change is one of the major concerns worldwide, but it is significantly important in developing countries where there is a lack of access to secure water sources. All over the world, ground water basins are over-exploited and water quality is declining. (UN-Water, 2015) (UNESCO, 2012). With the current rate of increase in population, industrialization and urbanization, there is an increase in volume of wastewater generated. For this large volume, the conventional treatment methods are becoming more time and energy consuming and sometimes failing leading to pollution of water bodies. Reuse of this treated wastewater is an important alternative to reduce the pressure on over-exploited resources (Capocelli, 2018). Some reuse of this water for irrigation usages in urban and peri-urban areas is seen in recent times to save water (Rajasulochana, 2016).

Wastewater is characterised by various parameters like temperature, pH, dissolved oxygen (DO), turbidity, Bio-Chemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), phosphates, nitrates, colour, metals, faecal coliforms etc. Most of the wastewater treatment plants use the conventional method of sedimentation-filtration-flocculation. The most common problem faced by these plants is that they have a large retention time hence they require large space for treatment. Since 1990, there has been tremendous increase in our scientific knowledge. This has helped us to understand the various long-term effects of discharging this wastewater in a better manner. There is a greater awareness regarding the various health issues which may arise because of releasing toxic and potentially toxic chemicals in the environment (Bakkaloglu, 1998). The limitations of the conventional methods

can be listed as larger space, time and energy required. Large areas required for treatment make it a costly process. Chlorine was proficient in destroying various bacteria, viruses, and protozoa, including pathogens like Salmonella, Shigella, and Vibrio cholera (Blaney, 2014). However, studies have demonstrated that chlorine, when reacting with organic matter, produces carcinogenic disinfection by-products such as tri-halomethanes and halo-acetic acids (C. O. Lee et al., 2012). These by-products have adverse effects on both public health and aquatic life. Water bodies receiving municipal wastewater treated with chlorine have reported fish kills, as chlorine and chlorine-ammonia compounds are toxic to various freshwater fish species (Maya et al., 2018, Nasuhoglu et al., 2018). Environmental concerns related to chlorine also point towards change from conventional oxidation to accelerated oxidation process.

Scenario in India: It is estimated that the projected wastewater from urban centres may cross 120,000 MLD by 2051 and that rural India will also generate not less than 50,000 MLD in view of water supply designs for community supplies in rural areas generation. Central Pollution Control Board (CPCB) studies depict that there are 269 sewage treatment plants (STPs) in India, of which only 231 are operational, thus, the existing treatment capacity is just 21 per cent of the present sewage generation.

Scenario in Maharashtra: With a population of 124.7 million, Maharashtra is the second largest state in India, by population. According to Central Pollution Control Board, in 2006, Maharashtra generated 9,986 MLD of wastewater in 50 class I cities. Sewage treatment capacity is reported as 4,225 MLD and nearly 58 per cent untreated wastewater is discharged into downstream water bodies. In 2010-11, a performance audit carried out by CAG noted that, "domestic effluents in the state are inadequately treated". Scrutiny of the State Pollution Control Board records reveals that only 8 out of 150 local bodies provided STPs; in 18 out of 25 cities, domestic effluents were discharged without any treatment and in 7 (except Navi Mumbai) the gap between sewage generation and treatment capacity was in the range of 48 to 94 per cent (CAG, 2011).

Scenario in Mumbai: The city has seven wastewater treatment plants with preliminary treatment facilities at Worli, Ghatkopar, Bhandup, Versova, Colaba, Bandra and Malad. Institutional wastewater is the principal source of sewage in Mumbai. The city gets 3,800 MLD. According to official records, 2,100 MLD of water goes to the sea as sewerage. Available sewage treatment capacity is 1998 MLD, where 1700 MLD sewage is collected for treatment. Out of 62 STPs, 4

STPs have treatment capacity of more than 200 MLD and 48 STPs have treatment capacity less than 1 MLD.

The urgent call for a master plan and new facilities was the driving force behind the Mumbai Sewage Disposal Project (MSDP). The project, funded with assistance from the World Bank, is expected to strengthen the capacity of Water Supply and Sewerage Department of the Municipal Corporation of Greater Mumbai (MCGM) to manage and deliver sewage services. It aims to improve the health and environmental condition in Greater Mumbai for all residents, and restore the quality of surrounding coastal waters and creeks. The total treatment capacity planned in 2025 is for an average dry weather flow of 2,600 MLD (Water world, 2002)

BMC has necessitated that all the new constructions should have their own sewage treatment plant. The main reason behind this initiative is that the municipal authorities are unable to handle the large amounts of waste generated. As more and more population is being added up, the current resources or treatment facilities are not sufficient to handle these volumes efficiently. Hence, all the new constructions need to have their own treatment facilities. Such wastewater treatment plants should be capable of handling the sewage generated. This leads to an additional expense in terms of land required, energy and labor required and cost of treating the water. Most buildings prefer to have such WTPs in the basement so as to avoid the nuisance of foul odour, and pests etc.

This research aims to observe the effect of various doses of ozone on the following parameters – pH, BOD, COD, turbidity, Total Dissolved Solids (TDS), and Suspended Solids (SS). The effect of ozone on various other parameters like PPCPs and EDCs are not considered here due to time and other constraints. Here, the effects of ozonation and hydrogen peroxide will be considered as a stand-alone treatment so as to check replace ability of STPs in individual, residential and commercial buildings so as to have ease of operation, savings in time, area required and cost of treatment.

3.3 Ozone as AOP

Ozone is a highly reactive chemical having a high oxidation reduction potential of 2.07V (Hoigne, 1998). Hence it has been widely used for drinking water disinfection. Ozone finds use in other industries like textile, paper and pulp, cooling waters, medical therapies, etc. Interest in ozone has been increasing over the past years. The need to achieve higher effluent qualities and greater compliance with physico-chemical and microbiological quality standards before discharge has stimulated the use of ozone in the treatment of municipal waste water effluents.

The main objective being colour removal, decrease in Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), disinfection and degradation of micro- pollutants (Paraskeva & Graham, 2002). Several applications for treatment of municipal and industrial waste water have been studied. Most of these studies have used ozonation in combination with activated sludge treatment (Gonzalez et al., 2003) or using activated carbon and ozonation in combination (Hollender et al., 2009).

A wide variety of Pharmaceutical and Personal Care Products (PPCPs), Endocrine Disrupting Compounds (EDCs), pesticides and solvents are also deposited in the sewers and find their way to Sewage Treatment Plants (STPs). The presence of such micro-pollutants endangers the reuse of treated waste water (Castigleoni et al., 2006). Also, many of these substances escape to conventional activated sludge waste water treatments allowing them to reach the surface water streams and distribute in the environment (Tauxe-Wuersch et al., 2005)

COD is a measure of the amount of oxygen required to oxidize the organic matter in a sewage sample by chemical oxidation. Higher the COD, more the oxygen stripping capacity the discharged effluent will have when discharged into receiving water. Various types of effluents require a different amount of oxygen to reach a stable stage. Ozone provides this amount of oxygen. Depending on age of effluent and type and amount of pollutant present, the ozone dosage will vary. Domestic sewage generally has a COD of about 600-900 mg/L and are treated to at least 75-100 mg/L. Industrial effluents have a much higher value of 167-8220 mg/L (Nirgude et al., 2013). The organic content of the effluent (expressed by COD and SS) is commonly used as an indicator of ozone dose required for the effluent. Table 3.1 below provides a summary of COD reduction by ozone treatment of secondary effluents.

Table 3.1: Summary of COD reduction by ozone treatment of secondary effluents (Paraskeva & Graham, 2002)

Source	Ozone dose (mg/L)	Initial COD (mg/L)	Final COD (mg/L)	Percentage reduction
Gardiner and Montgomery (1968)	5-41	260-560	Reduction of approximate 50% ozone dose	
Nebel et al. (1973)	12-16	200-400		23
Fressonnet (1983)	6-9	200-350	15-30	
Legube et al. (1987)	6-12	330-750		25
Absi et al. (1993)	14	400-570		50
Toffani & Richardson (1995)	20	120-200		30-50
Sasai et al. (1997)	15	200	13	33
Paraskeva et al. (1998)	2.5-5	220-490		30-50

Due to the shortcomings of chlorinated effluents, alternative disinfection methods have been explored. Ozone and Ultra-Violet (UV) treatment have emerged as viable alternatives, drawing from their successful application in drinking water treatment.(Friedrich et al., 2009) Use of ozonation for improvement in BOD, COD, colour and turbidity for municipal wastewaters showed promising results (Sallanko & Okkonen, 2009). As a chemical oxidation agent, ozone can effectively remove both colour and odour from water and gas stream and it produces less byproducts compared to chlorine-based oxidation. However, ozone alone is less effective for general COD removal because its degradation of carbon-carbon covalent bonds is not that high, hence often a combination of ozone and hydrogen peroxide is often used (E. Lee et al., 2011). As a disinfectant, the effectiveness of ozone depends on the susceptibility of the target organisms, the contact time, and the concentration of the ozone. (US EPA, 1999). The advantages and limitations of using ozone have already been covered in section 1.3.1

3.4 Hydrogen peroxide as AOP

Hydrogen peroxide is being used to reduce BOD, COD, offensive odor and foaminess in domestic wastewater since many years. While the cost of chemical oxidization is typically more than that through the physical or biologic means, hydrogen peroxide can be used as an autonomous treatment or as an improvement of existing physical or biologic treatment processes,

according to the situation. Hydrogen peroxide can be used alone or with a catalyst such as iron (Fe2+ or Fe3+), UV light, ozone (O_3), catalytic autoxidation and the alkali contribute to the reduction of the BOD/COD in the wastewater (Ksibi, 2006). The advantages and limitations of using hydrogen peroxide have already been covered in section 1.4.1

3.5 Use of WQI

The methods used for the calculation of WQI are described in detail as follows:

1. NSFWQI:

NSFWQI is a qualitative reduction indicator. Based on a survey of a large number of specialists with different specializations in the field, initially, 35 contaminants were analyzed but then 9 parameters were selected for formulating the main index. These nine parameters were temperature, dissolved oxygen, biochemical oxygen demand, acidity, nitrate, total phosphorus, total soluble solids, faecal coliform, and turbidity (Javadinejad et al., 2021). It is widely used to evaluate the WQI of water bodies. The major disadvantage is that it does not account for water use capacities and ignores all types of water consumption in the evaluation process (Chidiac et al., 2023).

The mathematical expression used is as follows

$$\mathrm{NSFWQI} = \sum_{i=1}^{n} \mathrm{QiWi}$$

Where Q_i is the sub-index for the ith water quality parameter. Wi is the weight associated with ith water quality parameter. N is the number of water quality parameter.

This method gives WQI values in ranges from 0 to 100, where 100 represents perfect water quality conditions, while zero indicates water that is not suitable for the use and needs further treatment (Samadi et al., 2015). Table 3.2 gives the classification of water quality based on NSFWQI.

Table 3.2:Classification of water using NSFWQI (Chidiac et al., 2023)

Numerical value index	Definition
26–50	Bad
51–70	Moderate
71–90	Good
91–100	Excellent

2. WAWQI:

The weighted arithmetic index is used to calculate the treated water quality index, in other terms, this method classifies the water quality according to the degree of purity. It consists of three steps.

a. quality rating or sub-index was calculated using the following equation

$$Qn = 100 \times \frac{[Vn - Vo]}{[Sn - Vo]}$$

where, Qn is the quality rating for the nth water quality parameter.

Vn is the observed value of the nth parameter at a given sampling station.

Vo is the ideal value of the nth parameter in a pure water.

Sn is the standard permissible value of the nth parameter.

b. unit weight was calculated by a value inversely proportional to the recommended standard values (Sn) of the corresponding parameters

$$Wn = \frac{K}{Sn}$$

where, Wn is the unit weight for the nth parameter.

K is the constant of proportionality.

Sn is the standard value of the nth parameter.

c. Overall WQI is the aggregation of the quality rating (Qn) and the unit weight (Wn) linearly

$$WQI = \frac{\sum Qn\ Wn}{\sum Wn}$$

This method gives WQI values in ranges from 0 to 100, where 0 represents excellent water quality conditions, while 100 indicates water that is not suitable for the use and needs further treatment. Table 3.3 below gives the quality of water based on the values of WAWQI

Table 3.3: WAWQI and status of water quality (Chidiac et al., 2023)

Water quality index level	Water quality status
0–25	Excellent water quality
26–50	Good water quality
51–75	Poor water quality
76–100	Very poor water quality
> 100	Unsuitable for drinking

For this study, WAWQI and NSFWQI were calculated for all the four sites using both ozone and hydrogen peroxide as means of AOP. The improvement in the values of WQI are shown in the next chapter.

Chapter 4. RESULTS AND DISCUSSIONS

4.1 General

This chapter deals with the test results obtained during the study and discussions related to the same. Grab samples of raw screened domestic wastewater are collected from four different sites for the purpose of testing, two are educational buildings and two are residential buildings. The samples were collected in one-liter bottles at various times of the day to account for the variation in the influent characteristics. The industrial-grade reagents and chemicals used for the testing were sourced from Loba Chemie Pvt. Ltd., Mumbai, India. The variation in the values of various parameters due to ozonation as well as hydrogen peroxide are observed.

4.2 Effect of ozonation on various parameters

Figure 4.1a and b show the oxygen concentrator and ozone generator used in the study. The oxygen concentrator concentrates the oxygen from air and passes it to the ozone generator where oxygen is converted to ozone by means of electrical sparks. Ozone was added for time intervals varying from 2 minutes to 25 minutes at concentrations of 30 mg/L and 14 mg/L and the reduction in parameters was observed. These reductions are shown graphically in Figure 4.2 below.

Figure 4.1a: Oxygen concentrator

Figure 4.1b: Ozone generator

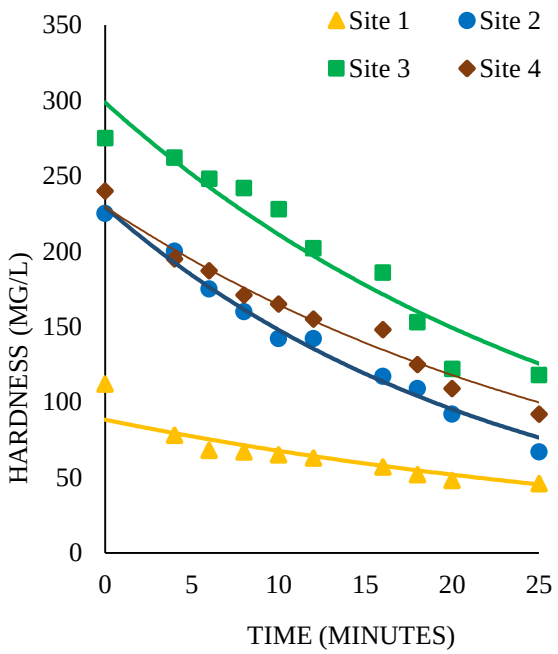

Figure 4.2.1a: Variation in hardness due to 30 mg/lit of ozone

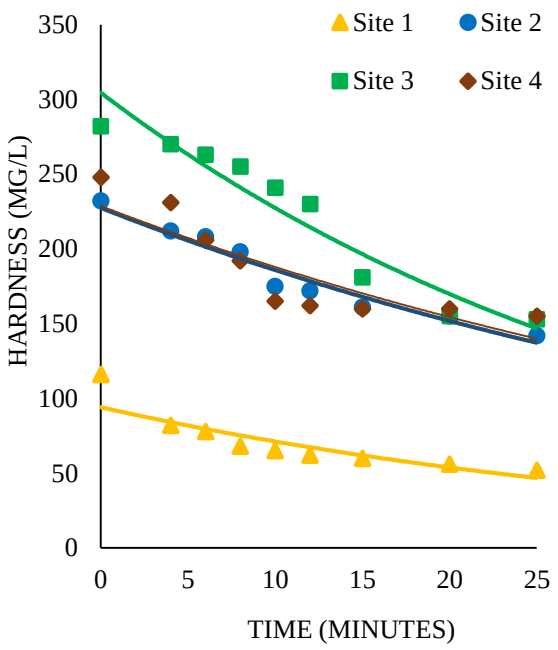

Figure 4.2.1b: Variation in hardness due to 14 mg/lit of ozone

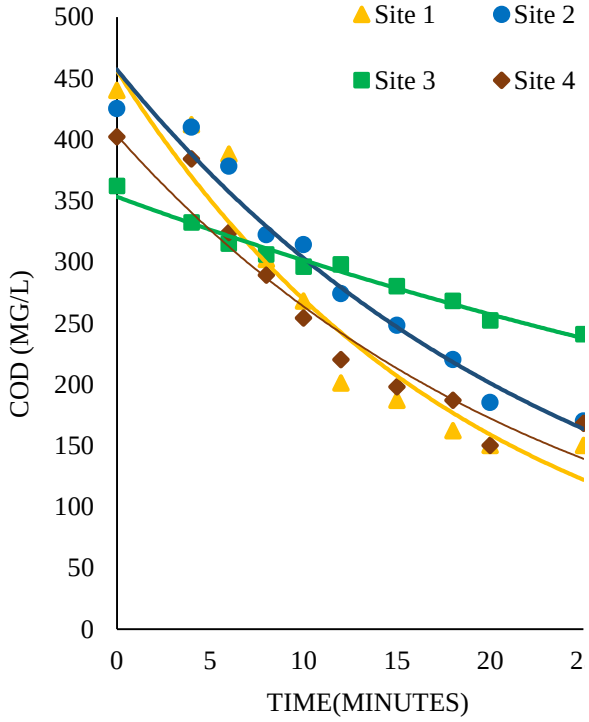

Figure 4.2.2a: Variation in COD due to due to 30 mg/lit of ozone

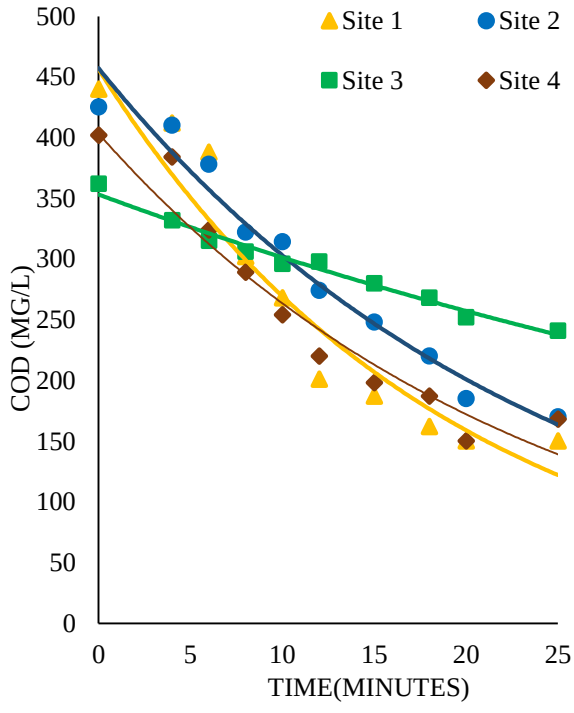

Figure 4.2.2b: Variation in COD due to 14 mg/lit of ozone

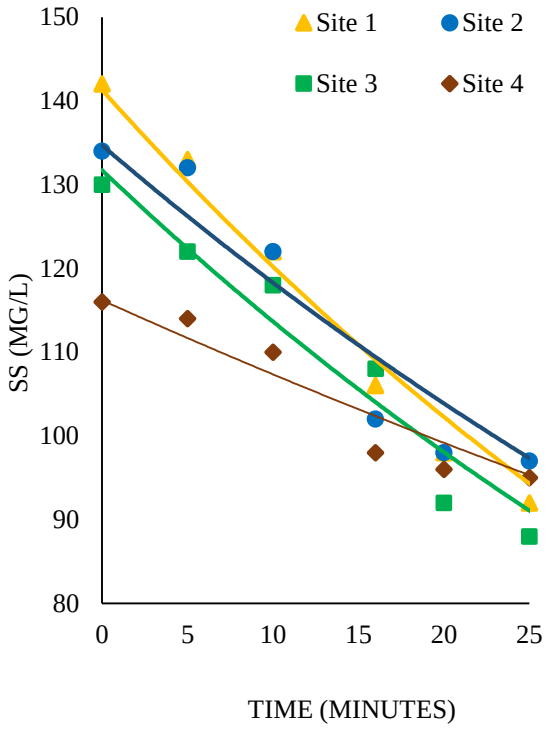

Figure 4.2.3a: Variation in SS due to 30 mg/lit of ozone

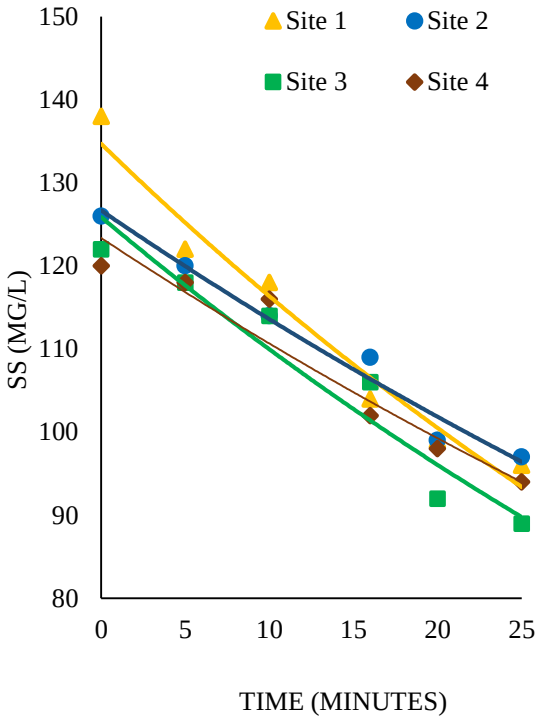

Figure 4.2.3b: Variation in SS due to 14 mg/lit of ozone

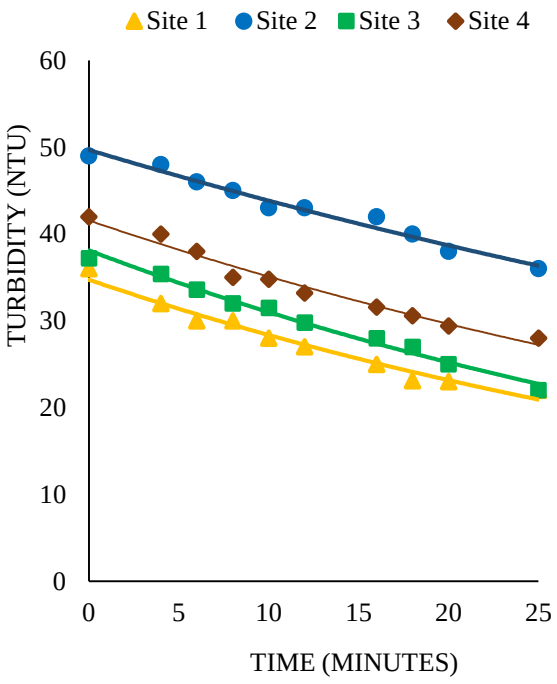

Figure 4.2.4a: Variation in turbidity due to 30 mg/lit of ozone

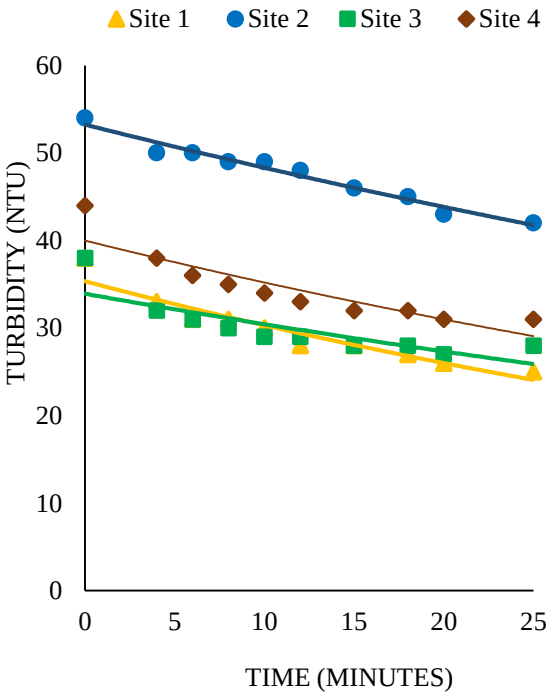

Figure 4.2.4b: Variation in turbidity due to 14 mg/lit of ozone

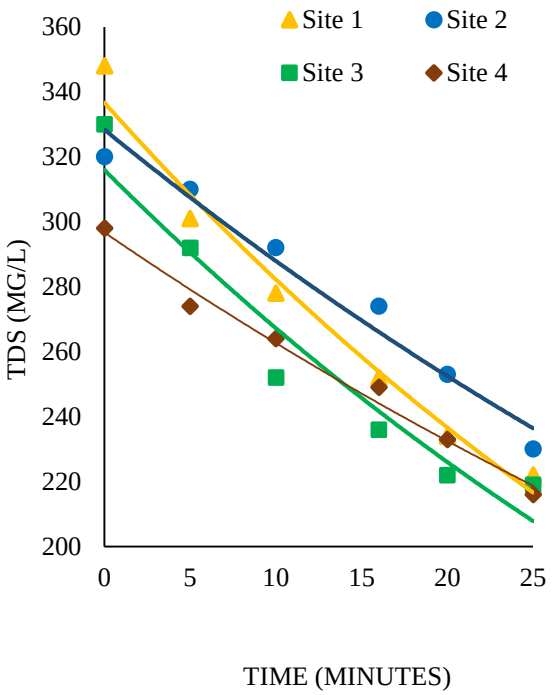

Figure 4.2.5a Variation in TDS due to 30 mg/lit of ozone

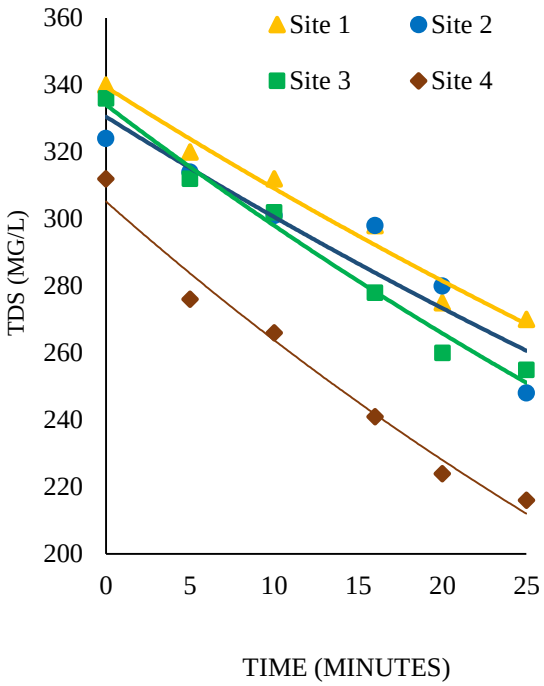

Figure 4.2.5b Variation in TDS due to 14 mg/lit of ozone

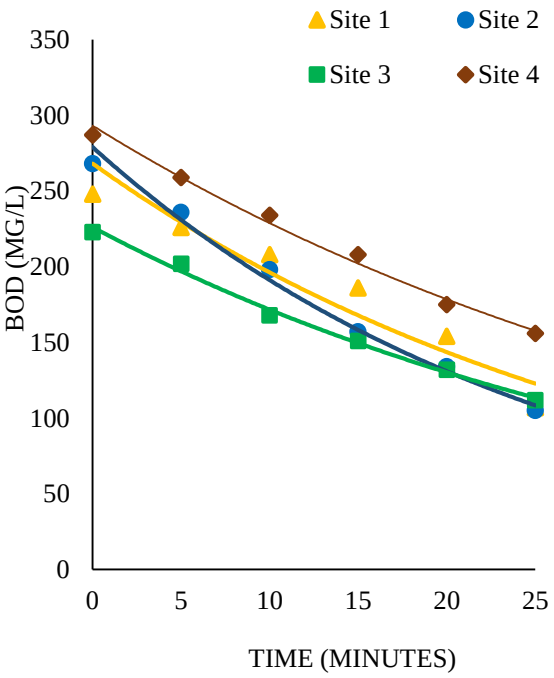

Figure 4.2.6a: Variation in BOD due to 30 mg/lit of ozone

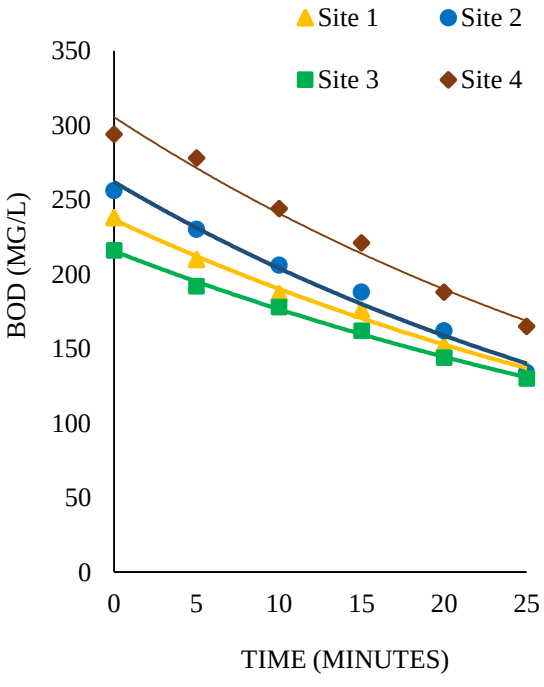

Figure 4.2.6b: Variation in BOD due to 14 mg/lit of ozone

Figure 4.2 Reduction in parameters due to ozonation

4.3 Effect of hydrogen peroxide on various parameters

The tests conducted on wastewater using ozone is repeated using hydrogen peroxide in varying quantities on four sites as earlier. 5 ml/L and 10 ml/L of 30% hydrogen peroxide was used and the samples were tested 30, 60, 90 and 120 minutes after the addition of hydrogen peroxide. The results are shown in Figure 4. 3 below

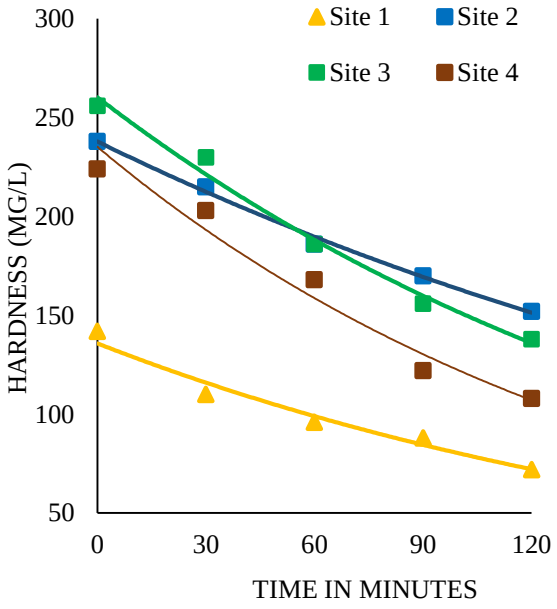

Figure 4.3.1a: Variation in hardness due to 5ml/lit of 30% hydrogen peroxide

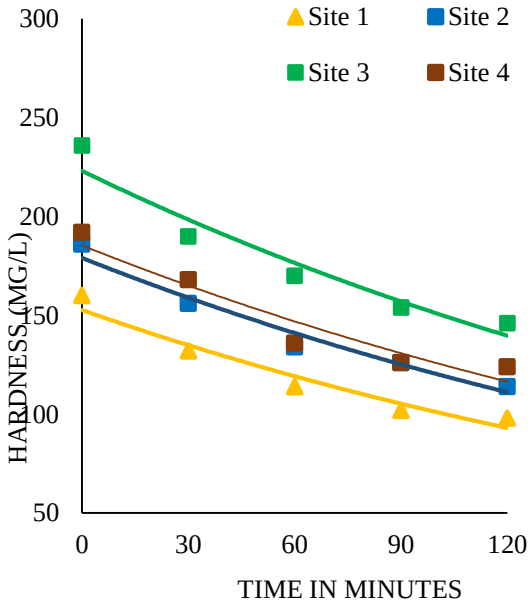

Figure 4.3.1b: Variation in hardness due to 10ml/lit of 30% hydrogen peroxide

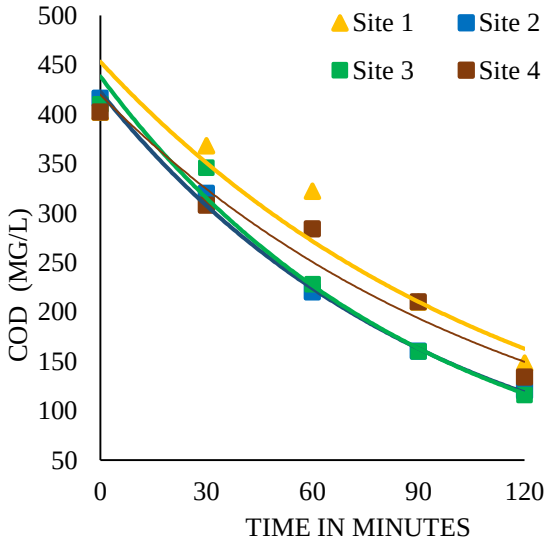

Figure 4.3.2a: Variation in COD due to 5ml/lit of 30% hydrogen peroxide

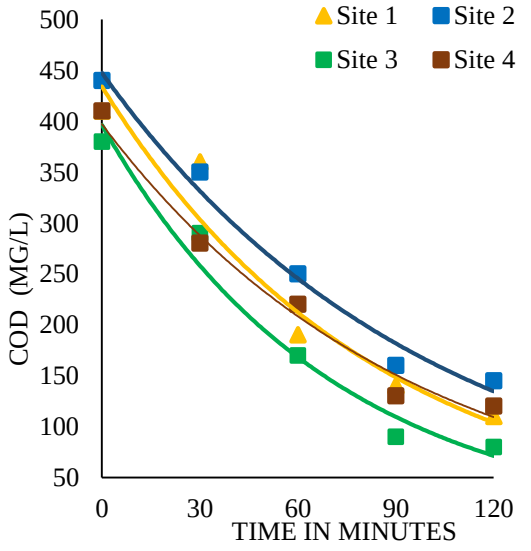

Figure 4.3.2b: Variation in COD due to 10ml/lit of 30% hydrogen peroxide

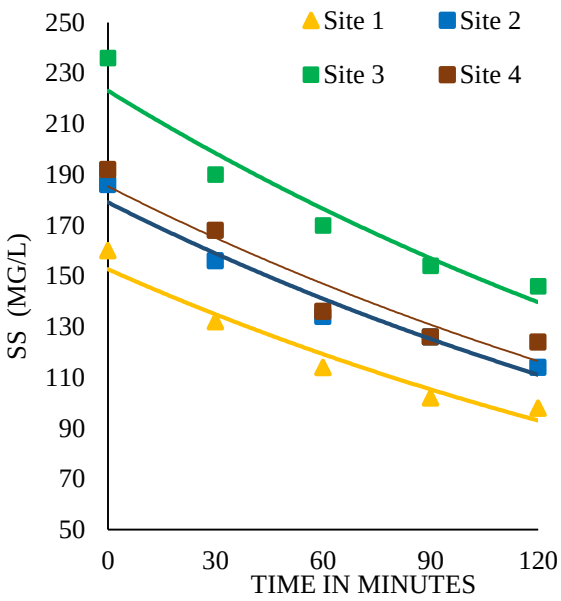

Figure 4.3.3a: Variation in SS due to 5 ml/lit of 30% hydrogen peroxide

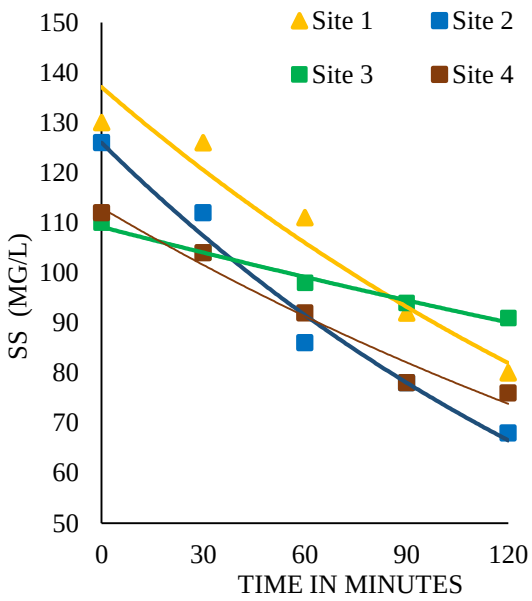

Figure 4.3.3b: Variation in SS due to 10 ml/lit of 30% hydrogen peroxide

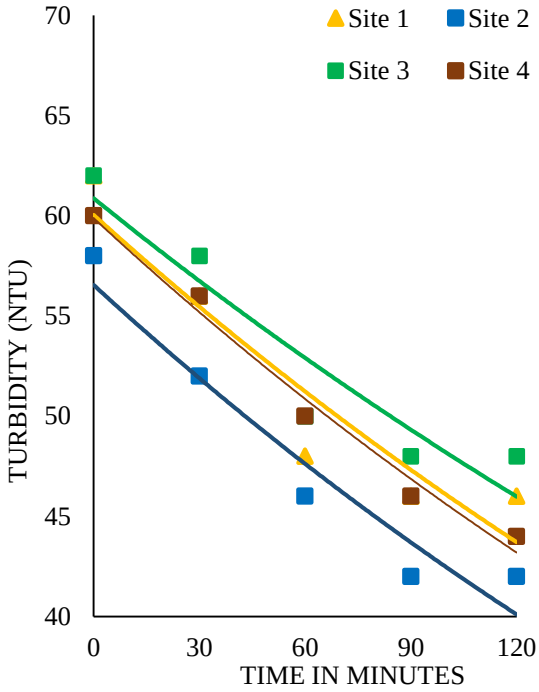

Figure 4.3.4a: Variation in turbidity due to 5 ml/lit of 30% hydrogen peroxide

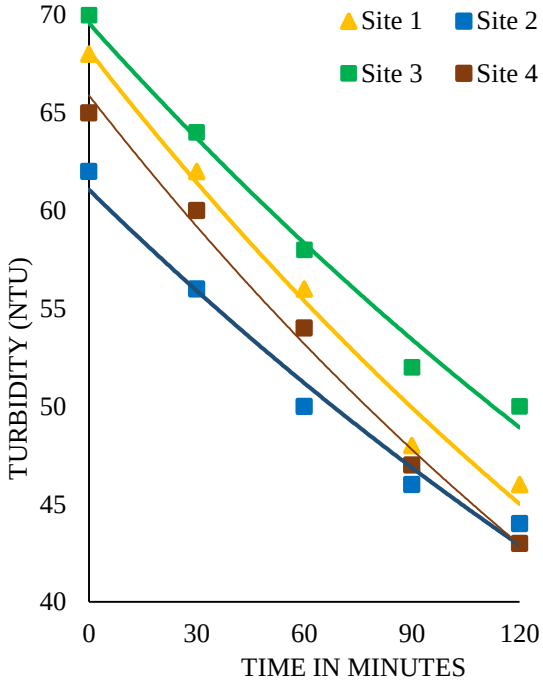

Figure 4.3.4b: Variation in turbidity due to 10 ml/lit of 30% hydrogen peroxide

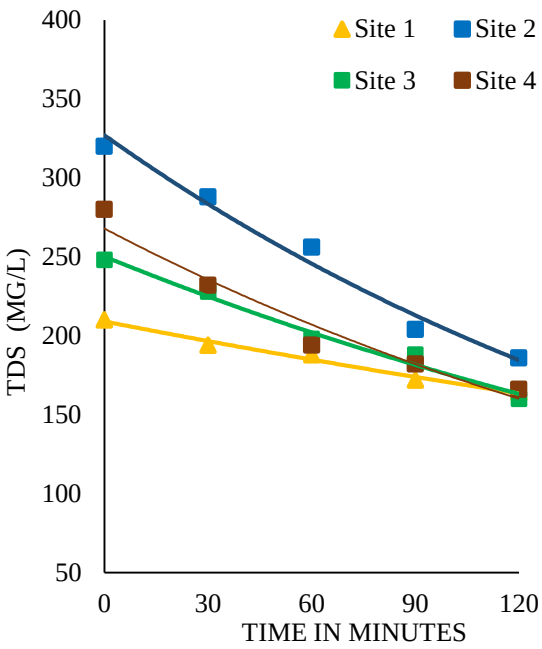

Figure 4.3.5a Variation in TDS due to 5ml/lit of 30% hydrogen peroxide

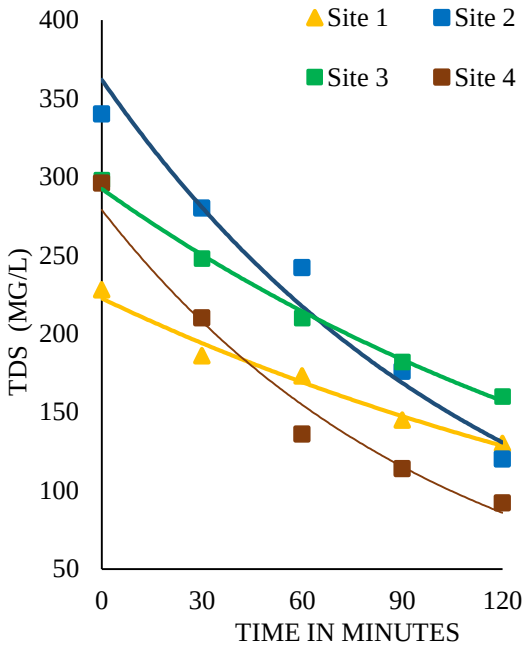

Figure 4.3.5b Variation in TDS due to 10ml/lit of 30% hydrogen peroxide

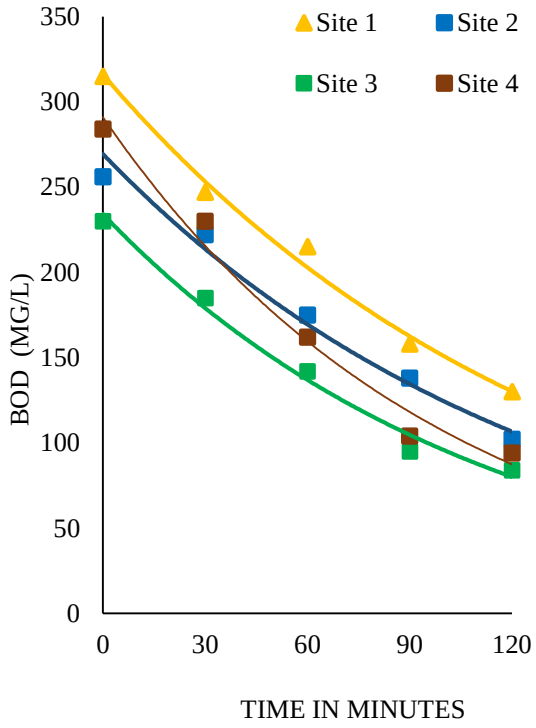

Figure 4.3.6a: Variation in BOD due to 5ml/lit of 30% hydrogen peroxide

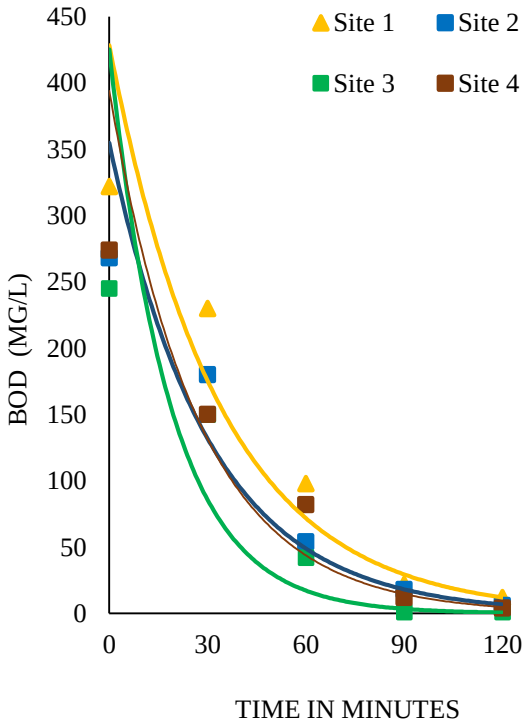

Figure 4.3.6b: Variation in BOD due to 10 ml/lit of 30% hydrogen peroxide

Figure 4.3 Reduction in parameters due to hydrogen peroxide

Due to the addition of ozone and hydrogen peroxide, there is a definite improvement in the parameters tested. WQI is calculated using NSFWQI and WAWQI methods for raw water at all the four sites and also after treatment using ozone and hydrogen peroxide. Sample calculations for site 1 are shown below in tables 4.1, 4.2 and 4.3 for hydrogen peroxide using WAWQI methods. Calculations for all the sites and for both the methods will be added up in the thesis.

Table 4.1: Calculation for NSFWQI of raw water of site 1

Parameter	measured value Vn	Std. value	Qn	W=k/ Sn	weighted values
		Sn	(Vn/Sn)*100		WiQi
COD	402	250	160.80	0.08	13.59
SS	130	100	130.00	0.21	27.46
BOD	315	30	1050.00	0.70	739.44
			TOTAL	1.00	780.49

Table 4.2: Calculation for NSFWQI for site 1 when using 5 ml/l of hydrogen peroxide

Parameter	measured value Vn	Std. value	Qn	W=k/ Sn	weighted values
		Sn	(Vn/Sn)*100		WiQi
COD	148	250	59.20	0.08	5.00
SS	80	100	80.00	0.21	16.90
BOD	130	30	433.33	0.70	305.16
			TOTAL	1.00	327.07
% reduction=		58.09447			

Table 4.3: Calculation for NSFWQI for site 1 when using 10 ml/l of hydrogen peroxide

Parameter	measured value Vn	Std. value Sn	Qn (Vn/Sn)*100	W=k/ Sn	weighted values WiQi
COD	110	250	44.00	0.08	3.72
SS	98	100	98.00	0.21	20.70
BOD	12	30	40.00	0.70	28.17
			TOTAL	1.00	52.59
	% reduction=		93.46867858		

The reduction in the values of WQI due to ozonation and hydrogen peroxide have been calculated by using WAWQI methods. These have been summarized and shown in the tables 4.4 to 4.7 below.

Table 4.4: Reduction in WQI due to ozonation using WAWQI method

	SITE 1	SITE 2	SITE 3	SITE 4
WQI of raw water	627.03	570.55	768.08	711.8
Final WQI using 24mg/L of ozone/litre of wastewater	266.18	272.38	424.19	388.97
% reduction using 24mg/L of ozone/litre of wastewater	57.45	52.25	41.75	45.35
WQI of raw water	602.71	641.92	545.05	729.08
Final WQI using 14mg/L of ozone/litre of wastewater	344.60	340.79	332.11	412.86
% reduction using 14mg/L of ozone/litre of wastewater	42.82	46.91	39.06	43.37

Table 4.5: Reduction in WQI due to ozonation using NSFWQI method

	SITE 1	SITE 2	SITE 3	SITE 4
WQI of raw water	21.8	20.2	22.0	21.6
Final WQI using 24mg/L of ozone/litre of wastewater	27.6	24.0	27.8	25.8
% reduction using 24mg/L of ozone/litre of wastewater	26.6	18.85	26.36	19.44
Final WQI using 14mg/L of ozone/litre of wastewater	25.2	24.8	25.6	25.8
% reduction using 14mg/L of ozone/litre of wastewater	20.0	16.98	16.36	19.44

Table 4.6: Reduction in WQI due to hydrogen peroxide using WAWQI method

	SITE 1	SITE 2	SITE 3	SITE 4
WQI of raw water	780.49	641.62	577.00	703.92
Final WQI using 5ml hydrogen peroxide /litre of wastewater	327.07	257.86	220.33	241.24
% reduction using 5ml hydrogen peroxide /litre of wastewater	58.09	59.81	61.81	65.73
Final WQI using 10ml hydrogen peroxide /litre of wastewater	52.59	43.07	33.55	39.64
% reduction using 10ml hydrogen peroxide /litre of wastewater	93.04	93.15	94.17	93.84

Table 4.7: Reduction in WQI due to hydrogen peroxide using NSFWQI method

	SITE 1	SITE 2	SITE 3	SITE 4
WQI of raw water	21.4	19.4	18.6	18.6
Final WQI using 5ml hydrogen peroxide /litre of wastewater	24.6	24.0	23.6	23.8
% improvement using 5ml hydrogen peroxide /litre of wastewater	14.9	23.7	26.9	27.9
Final WQI using 10ml hydrogen peroxide /litre of wastewater	42.4	53.4	53.0	53.6
% improvement using 10ml hydrogen peroxide /litre of wastewater	101.9	187.1	194.4	194.5

Similar calculations for all the sites using NSFWQI and WAWQI methods for both ozone and hydrogen peroxide will be added in the thesis.

Chapter 5. CONCLUSION

Both ozone and hydrogen peroxide show a promising reduction in the parameters tested. The quantification of the improvement is done by calculating the WQI. WQI is generally used as a means to assess the quality of surface waters. In this study, WQI is used as a measure of the effectiveness of the treatment process. For ozone, two different concentrations namely 24 and 14 mg/L were used. The reduction percentage for ozone is in the range of 41 to 57% using the WAWQI method when 30 mg/L of ozone is used whereas this percentage is between 39 and 46% when 14 mg/L is used. When NSFWQI is calculated for 30mg/L of ozone, the improvement in WQI ranges from 19 to 26% whereas it varies from 16-20% when 14 mg/L is used.

Similarly, hydrogen peroxide is used in two different quantities namely 5ml/L and 10 ml/L. The reduction percentage is in the range of 58 to 66% using the WAWQI method when 5 ml/L is used whereas this percentage is between 93 and 94% when 10 ml/L is used. When NSFWQI is calculated for hydrogen peroxide, the improvement in WQI ranges from 15 to 28% for 5 ml/L whereas it varies from 102 to 195% when 10 ml/L is used.

The reduction in the parameters show a promising solution to the treatment of wastewater using AOPs. The time required is much lesser with AOPs as compared to conventional aeration. Space savings will be achieved as the area required for ozone generators is small as compared to aeration tanks. Also, addition of hydrogen peroxide can result in lesser space. Though turbidity shows that use of only AOP cannot serve as a replacement to the secondary stage of treatment, an additional stage of sand filter may be added up to reach an acceptable limit for this parameter also. Space savings will be achieved as the area required for ozone generators is small as compared to aeration tanks. Also, addition of hydrogen peroxide can result in lesser space requirement for the treatment.

Chapter 6. FUTURE SCOPE

Inclusion of all the parameters for the calculation of WQI can be considered as a future scope for the study. Also, the cost implications of using AOPs can be considered as a scope for future work.

Chapter 7. PUBLICATIONS

JOURNAL PAPERS:

- Shrivastava Preeti R., Mategaonkar Meenal; "Wastewater Remediation Using Advanced Oxidation Processes (AOP)", *Water Quality Research Journal*. https://doi.org/10.2166/wqrj.2024.114
- Shrivastava Preeti R., Mategaonkar Meenal; "Case study on Water Quality Index for Wastewater Treatment in Mumbai", *Water Practice and Technology*, (2024) 19 (4): 1177–1184. https://doi.org/10.2166/wpt.2024.081

BOOK CHAPTER:

- Shrivastava Preeti R., Mategaonkar Meenal; "Sustainability and Innovations in Civil Engineering" book chapter on "Sustainable Techniques for Domestic Wastewater Treatment: A Review" published by Imperial Publications, Mumbai ISBN: 978-93-91044-60-2

CONFERENCES:

- Shrivastava Preeti R., Mategaonkar Meenal; "Impact of Advanced Oxidation Processes on wastewater treatment," *International Conference on Water and Sustainable Development 2024*, VNIT, Nagpur…to be held on 8th and 9th November, 2024. Papers will be published in Scopus indexed journal
- Shrivastava Preeti R., Vichare Shrish; "Ozonation as a technique for wastewater treatment," Proceedings of *4th International Conference on Materials, Mechanics and Management* organized by Government College of Engineering, Trivandrum held during March 2020 ISBN no. 978-93-89105-41-4
- Shrivastava Preeti R., Vichare Shirish; "Review of Techniques Currently Used for Treatment of Domestic Wastewater," *International Journal of Engineering and Technology*: ISSN no. 2247-524X, vol. 7, no.4.41, 2018, pp:188-191

Chapter 8. REFERENCES:

Bakkaloglu, I., Butter, T. J., Evison, L. M., Holland, F. S., & Hancock, I. C. (1998). Screening of various types biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption, sedimentation and desorption. *Water Science and Technology*, *38*(6), 269–277. https://doi.org/10.2166/wst.1998.0261

Blaney, L. (2014). Ozone Treatment of Antibiotics in Water. In *Water Reclamation and Sustainability* (pp. 265–316). Elsevier. https://doi.org/10.1016/B978-0-12-411645-0.00012-2

Castigleoni, S. ., Fanelli, R., Bagnati, R., Pomati, F. ., Calamari, D. ., & Zuccato, E. (2006). Removal of pharmaceuticals in sewage treatment plants in Italy. *Journal of Environment, Science and Technology*, *4*, 357–363.

Chidiac, S., El Najjar, P., Ouaini, N., El Rayess, Y., & El Azzi, D. (2023). A comprehensive review of water quality indices (WQIs): history, models, attempts and perspectives. *Reviews in Environmental Science and Bio/Technology*, *22*(2), 349–395. https://doi.org/10.1007/s11157-023-09650-7

Deng, Y., & Zhao, R. (2015). Advanced Oxidation Processes (AOPs) in Wastewater Treatment. In *Current Pollution Reports* (Vol. 1, Issue 3, pp. 167–176). Springer. https://doi.org/10.1007/s40726-015-0015-z

Friedrich, E., Pillay, S., & Buckley, C. A. (2009). = *Water SA (on-line) 73 Environmental life cycle assessments for water treatment processes-A South African case study of an urban water cycle*. http://www.wrc.org.za

Gonzalez, P. ., Zaror, C. ., Carrasco, V. ., Mondaca, M. A. ., & Mansilla, H. (2003). Combined Physical-Chemical And Biological Treatment Of Poorly Biodegradable Industrial Effluents. *Journal Of Environmental Science And Health* , *38*(10), 2201–2208.

Hoigne, J. (1998). *The Handbook Of Environmental Chemistry: Quality And Treatment Of Drinking Water II: Hrubec, J. Ed; Springer-Verlag: Berlin; Vol. 5 Part C.: Vol. 5 part C* (Springer-Verlag).

Hollender, J., Zimmermann, S. G., Koepke, S., Krauss, M., Mcardell, C. S., Ort, C., Singer, H., Von Gunten, U., & Siegrist, H. (2009). Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. *Environmental Science and Technology*, *43*(20), 7862–7869. https://doi.org/10.1021/es9014629

Javadinejad, S., Dara, R., Hamed, M. H., Saeed, M. A. H., & Jafary, F. (2021). Investigation of water quality in wet and dry seasons under climate change. *Resources Environment and Information Engineering*, *3*(1), 111–123. https://doi.org/10.25082/reie.2021.01.002

Ksibi, M. (2006). Chemical oxidation with hydrogen peroxide for domestic wastewater treatment. *Chemical Engineering Journal*, *119*(2–3), 161–165. https://doi.org/10.1016/j.cej.2006.03.022

Lazarova, V., Cirelli, G., Jeffrey, P., Salgot, M., Icekson, N., & Brissaud, F. (2000). Enhancement of integrated water management and water reuse in Europe and the Middle East. *Water Science and Technology*, *42*(1–2), 193–202. https://doi.org/10.2166/wst.2000.0313

Lee, C. O., Howe, K. J., & Thomson, B. M. (2012). Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. *Water Research*, *46*(4), 1005–1014. https://doi.org/10.1016/j.watres.2011.11.069

Lee, E., Lee, H., Kim, Y. K., Sohn, K., & Lee, K. (2011). Hydrogen peroxide interference in chemical oxygen demand during ozone based advanced oxidation of anaerobically digested livestock wastewater. *Iranian Journal of Environmental Health Science and Engineering*, *8*(2), 381–388.

Maya, N., Crispo, C., McFarland, V., Nasuhoglu, D., Isazadeh, S., Yargeau, V., & Metcalfe, C. D. (2018). Toxicity of extracts from municipal wastewater to early life stages of Japanese medaka (Oryzias latipes) to evaluate removals of micropollutants by wastewater treatment. *Environmental Toxicology and Chemistry*, *37*(1), 136–144. https://doi.org/10.1002/etc.3939

Mota, A. L. N., Albuquerque, L. F., Beltrame, L. T. C., Chiavone-Filho, O., Machulek, A., & Nascimento, C. A. O. (2008). Brazilian Journal of Petroleum and Gas Advanced Oxidation Processes and Their Application in the Petroleum Industry: a Review. *Brazilian Journal of Petroleum and Gas*, *3*, 122–142.

Nasuhoglu, D., Isazadeh, S., Westlund, P., Neamatallah, S., & Yargeau, V. (2018). Chemical, microbial and toxicological assessment of wastewater treatment plant effluents during disinfection by ozonation. *Chemical Engineering Journal*, *346*, 466–476. https://doi.org/10.1016/j.cej.2018.04.037

Nirgude, N. T. ., Shukla, S. ., & Venkatachalam, A. . (2013). Physico-Chemical Analysis Of Some Industrial Effluents From Vapi Industrial Area, Gujarat, India. *Rasayan Journal*, *6*(1), 68–72.

Pandis, P. K., Kalogirou, C., Kanellou, E., Vaitsis, C., Savvidou, M. G., Sourkouni, G., Zorpas, A. A., & Argirusis, C. (2022). Key Points of Advanced Oxidation Processes (AOPs) for Wastewater, Organic Pollutants and Pharmaceutical Waste Treatment: A Mini Review. In *ChemEngineering* (Vol. 6, Issue 1). MDPI. https://doi.org/10.3390/chemengineering6010008

Paraskeva, P. ., & Graham, N. (2002). Ozonation Of Municipal Waste Water Effluents. *Journal Of Water And Environment Research*, *74*(6), 569–581.

Sallanko, J., & Okkonen, J. (2009). Effect of ozonation on treated municipal wastewater. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, *44*(1), 57–61. https://doi.org/10.1080/10934520802515350

Samadi, M. T., Sadeghi, S., Rahmani, A., & Saghi, M. H. (2015). Survey of water quality in Moradbeik river basis on WQI index by GIS. *Environmental Health Engineering and Management Journal*, *2*(1), 7–11. https://core.ac.uk/download/pdf/33488133.pdf

Tauxe-Wuersch, A. ., De Alencastro, A. F. ., Grandjean, D. ., & Terradellas, J. (2005). Occurrence Of Several Acidic Drugs In Sewage Treatment Plants In Switzerland And Risk Assessment. *Journal Of Water Research*, *39*, 1761–1772.

US EPA. (1999). *Wastewater Technology Fact Sheet Ozone Disinfection*.